ENTROPY OF NONREGULAR CONDENSED SYSTEMS WITH POLYATOMIC IMPURITIES

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Abstract
Nonregular condensed systems with polyatomic impurity particles are considered in this paper. The calculation of the thermodynamic characteristics of the system, including the change in entropy of nonregular condensed systems upon the introduction of polarizable, charged polyatomic impurity particles is carried out. The change in the system's free energy and its dependence on temperature is calculated in order to determine the change in entropy of the system. A Green's function apparatus is used to perform the calculations.

Keywords: entropy, free energy, condensed systems, green functions, polyatomic impurities, Hamiltonian

Nonregular condensed systems with polyatomic impurity particles are considered [1 – 10]. This paper calculates the thermodynamic characteristics of the system, including the change in entropy of nonregular condensed systems [4 –7] upon the introduction of polarizable, charged polyatomic impurity particles. Naturally, to calculate the change in entropy of the system, it is necessary to calculate the change in the system's free energy and its dependence on temperature.

To calculate the thermodynamic characteristics of condensed systems with impurity particles, the apparatus of temperature Green functions for nonregular condensed systems is convenient, allowing one to take into account the effects of frequency and spatial dispersion of the system and the specifics of the interaction of impurity particles with the medium.

The total change in the free energy of nonregular condensed system upon the introduction of impurity particles includes the following components:

1. Work associated with the formation of the cavity containing the impurity particle.

2. Free energy associated with the translational and rotational motion of the particle as a whole.

3. Electrostatic energy associated with the interaction of the impurity particle with the medium.

As a rule, the last term contributes the largest change in the free energy of a system upon the introduction of an impurity into a condensed system. It is this change in the system's free energy that provides the main contribution to the change in the system's entropy, which is calculated in this work.

It must be taken into account that the temperature dependence of the free energy of the system is not only explicit but also implicit. In particular, the characteristic correlation lengths of polarization fluctuations in the medium of complex condensed systems depend on temperature. For a system model that takes into account the interaction of polarization fluctuations in the medium with the static field of an impurity particle, this dependence can be present through the temperature dependence of the system's permittivity.

1. Hamiltonian of nonregular condensed system with polyatomic impurity particle

The Hamiltonian of a system in which a charged impurity particle is located in a condensed medium can be represented as:

$$H = H^m + \mathcal{H}^p - \frac{1}{2}\int d\vec{r}\langle\vec{P}(\vec{r})\rangle\vec{E}(\vec{r},Q) - \int d\vec{r}\delta\vec{P}(\vec{r})\vec{E}(\vec{r},Q) \quad (1)$$

Here H^m - is the Hamiltonian of polarized medium, $\mathcal{H}^p$ is the Hamiltonian of the impurity particle, $\langle\vec{P}(\vec{r})\rangle$ - is the average polarization of the medium, $\delta\vec{P}(\vec{r})$ - is fluctuation of polarization of the medium, $\vec{E}(\vec{r},Q)$ - is the electric field strength of the impurity, Q are the coordinates of the intramolecular vibrations of a particle.

According to the fluctuation-dissipation theory, the Fourier component over time of the average polarization of the system can be represented through the Green function as follows:

$$\langle\vec{P}(\vec{r},\omega)\rangle = -\int d\overrightarrow{r'}G_{P_\alpha P_\beta}\left(\overrightarrow{r},\overrightarrow{r'};\omega\right)E_\beta\left(\overrightarrow{r'};\omega\right) \quad (2)$$

where $G_{P_\alpha P_\beta}\left(\overrightarrow{r},\overrightarrow{r'};\omega\right)$ is the Fourier component over time of the Green function of the medium polarization operators.

After simple transformations, the Hamiltonian of the system can be represented as

$$H = \delta\Omega_0 + H^p + H^m + H^1_{int} + H^2_{int} \quad (3)$$

Here H^p - is the Hamiltonian of polarized particle, H^m is the Hamiltonian of polarized medium, H^1_{int} is the Hamiltonian of the interaction of polarization fluctuations of the medium with the static field of an impurity particle:

$$H^1_{int} = -\int d\vec{r}\delta\vec{P}(\vec{r})\overrightarrow{E_0}(\vec{r})\,;\ \overrightarrow{E_0}(\vec{r}) = \vec{E}(\overrightarrow{r},Q=Q_0) \quad (4)$$

In the formula (3) H^2_{int} is the Hamiltonian of the interaction of polarization fluctuations of the medium with intramolecular vibrations of the impurity

$$H^2_{int} = -\sum_n\int d\vec{r}\vec{v}_n(\vec{r})\,\delta\vec{P}(\vec{r})\delta Q_n \quad (5)$$

In formula (3) $\delta\Omega_0$ is the free energy of solvation of the particle, equal to

$$\delta\Omega_0 = \frac{1}{2}\int E_\alpha(\overrightarrow{r},Q=Q_0)\,G_{P_\alpha P_\beta}\left(\overrightarrow{r},\overrightarrow{r'};\omega=0\right)E_\beta\left(\overrightarrow{r'},Q=Q_0\right)d\vec{r}d\vec{r'} \quad (6)$$

The Hamiltonian H^m differs from the Hamiltonian of an unpolarized medium by the value

$$\delta F^m = \frac{1}{2}\int d\vec{r}\langle\vec{P}(\vec{r})\rangle\vec{E}(\vec{r},Q) \quad (7)$$

Within the framework of the linear response theory [4-5], the average polarization of the medium can be expressed through the strength of the electric field created by a polarized impurity particle, as a result for δF^m we have

$$\delta F^m = \frac{1}{2}\int E_\alpha(\vec{r},Q)\, G_{P_\alpha P_\beta}\left(\vec{r},\vec{r'};\omega = 0\right)E_\beta\left(\vec{r'},Q\right)d\vec{r}d\vec{r} \quad (8)$$

2. Free energy of nonregular condensed system with polyatomic impurity particle

The free energies of a condensed system with a polyatomic impurity particle $\delta\Omega_0$ and δF^m differ by the difference in the free energies of the impurity in the solvated state and in vacuum.

$$\delta\Omega_0 - \delta F^m = kTln\prod_{n=1}^{N} 2sh(\beta\omega_n/2) - kTln\prod_{n=1}^{N} 2sh(\beta\omega_{n0}/2) + J_0 \quad (9)$$

Where ω_n and ω_{n0} are frequencies of the n-th intramolecular vibration of the particle in a solvated state and in vacuum, J_0 is the difference between the minimal energies of a particle in a solvated state and in a vacuum.

As a result, the electrostatic part of the change in the free energy of the system, associated with the introduction of a polyatomic polarizable impurity particle into the condensed medium, is written in the form

$$\delta\Omega = \delta\Omega_0 + \delta F^m + \delta\Omega_1 + \delta\Omega_2 \quad (10)$$

where $\delta\Omega_1$ and $\delta\Omega_2$ are the changes in the free energy of the system associated with the interactions H_{int}^1 and H_{int}^2, and $\delta\Omega_0$ is free energy of solvation of a particle.

The retarded Green function of the polarization operators of the system in the case of the Debye approximation can be represented as

$$G^R\left(\vec{r},\vec{r'};\omega\right) = (C_0/4\pi)[\gamma_0/(\gamma_0 + i\omega)] \quad (11)$$

Where, γ_0 is a characteristic parameter of the system, and C_0 is a dimensionless constant equal to the difference between the reciprocals of the permittivities to the right and left (on the energy scale) of the corresponding absorption peak of the system.

3. Entropy of the system

If we do not take into account the temperature dependence of the correlation lengths of the polarization fluctuations of the medium on the temperature, then the change in the entropy of the system associated with the interaction of the polarization fluctuations of the medium with the static field of the impurity can be represented in the form

$$\delta S_1 = (\delta\Omega_1/C_0)(\partial C_0/\partial T) \quad (12)$$

where T is the temperature of the system.

The change in the entropy of a system caused by the interaction of polarization fluctuations of the medium with intramolecular vibrations of the impurity particle H_{int}^2, as well as the polarizability of the medium and impurity $\delta\Omega_0 + \delta F^m$ can be calculated for specific models of the Green functions of the medium's polarization fluctuation operators.

For the pole approximation of the Green function $G_{P_\alpha P_\beta}$, we obtain for the change in the entropy of the system:

$$\begin{aligned}\delta S_2 = {} & (k/2)ln[1-(U(0)/\omega_s)] - (kT/2)\left[1/\left(\omega_s - U(0)\right)\right]\sum_{i=1}^{m}(\partial/\partial T)\,(U_i/\omega_i) \\ & + kln\prod_{j=1}^{m+2}\Gamma\left[1-\left(\bar{\omega}_j/2\pi kT\right)\right] - kln\prod_{j=1}^{m}\Gamma[1-(\omega_i/2\pi kT)] \\ & - (1/2\pi)\sum_{j=1}^{m+2}\left\{\left[\left(\partial\bar{\omega}_j/\partial T\right) - \left(\bar{\omega}_j/T\right)\right]\psi\left[1-\left(\bar{\omega}_j/2\pi kT\right)\right]\right\} \\ & + (1/2\pi)\sum_{i=1}^{m}\{[(\partial\omega_i/\partial T) - (\omega_i/T)]\psi[1-(\omega_i/2\pi kT)]\} + k[ln(kT/\omega_s) - 1] \\ & + kln[2sh(\omega_s/2kT)] - (\omega_s/2T)\,cth(\omega_s/2kT) + (\partial J_0/\partial)\end{aligned} \quad (13)$$

Here, $\left[1-\left(\bar{\omega}_j/2\pi kT\right)\right]$ denotes the Γ -function, and $\left[1-\left(\bar{\omega}_j/2\pi kT\right)\right]$denotes the ψ function.

In formula 10.70, U(0) is the renormalized interaction of intramolecular vibrations of the impurity through the medium at zero frequency. For the pole approximation of the polarization fluctuation operators of the medium, the renormalized interaction is defined as

$$U(\omega_n) = \sum_{i=1}^{m}[u_i/(\omega_i - |\omega_n|)] \quad (14)$$

Here u_i and ω_i are experimental constants, m is the number of poles of the Green function of the operator of intramolecular vibrations of the impurity.

In formula 10.70, ω_s is the frequency of the intramolecular vibration of the impurity particle.

In formula 10.70, the derivatives $\partial\bar{\omega}_j/\partial T$cannot always be determined analytically. In this case $\partial\bar{\omega}_j/\partial T$ can be determined numerically, just like the frequencies.

For the Debye approximation of the frequency dependence of the Green function of the polarization operators of the medium for changes in the entropy of the system, we obtain

$$\delta S_2 = (\omega_s/2kT)ln(1-\acute{æ}) - (kT/2\,\omega_s)[1/(1-\acute{æ})][\partial U(0)/\partial T] + kln\prod_{j=1}^{3}\Gamma\left[1-\left(\overline{\omega}_j/2\pi kT\right)\right] - klnГ\left[1-(\gamma_0/2\pi kT)+kln[(kT/\omega_s)-1]\right] + kln2sh(\omega_s/2kT) - (\omega_s/2T)cth(\omega_s/2kT) - (1/2\pi)\sum_{j=1}^{3}\left[\left(\partial\overline{\omega_j}/\partial T\right)-\left(\overline{\omega_j}/T\right)\right]\psi\left[1-\left(\overline{\omega_j}/2\pi kT\right)\right] + [(\partial\gamma_0/\partial T)-(\gamma_0/T)]\psi[1-(\gamma_0/2\pi kT)] \quad (15)$$

Here, the coefficient of the coupling strength of intramolecular vibrations with the medium is equal to

$$\acute{æ} = -AC_0/4\pi \quad (16)$$

Here, the coefficient A for a spherically symmetric particle placed in a local homogeneous medium is equal to

$$A_{ss'} = -(8\pi/3r_0^3)C_0(\partial d/\partial Q)^2 = -(8\pi C_0/3r_0^3)\omega_0(\partial d/\partial q)^2 \quad (17)$$

where r_0 is the particle radius, ω_0 is the frequency of the intramolecular vibration, $\partial d/\partial q$ is the derivative dipole moment along the coordinate of the intramolecular vibration.

In an approximation in which the frequency dependence of attenuation on temperature can be neglected, for weak coupling with the medium, we have

$$\partial\overline{\omega_{2,3}}/\partial T = [\gamma_0\omega_s^2/2(\omega_s^2+\gamma_0^2)][\partial\acute{æ}(T)/\partial T] \mp i\omega_s[\gamma_0^2/2(\omega_s^2+\gamma_0^2)][\partial\acute{æ}(T)/\partial T] \quad (18)$$

For an impurity particle placed in a local homogeneous isotropic medium, the parameter has the form

$$[\partial\acute{æ}(T)/\partial T] = -A/2\pi\omega_s[(1/\varepsilon_r^2)(\partial\varepsilon_r/\partial T) - (1/\varepsilon_{st}^2)(\partial\varepsilon_{st}/\partial T)] \quad (19)$$

where ε_r and ε_{st} are the IR and static values of the permittivity of the medium.

Conclusion

Nonregular condensed systems with polyatomic impurity particles are considered. The thermodynamic characteristics of the system are calculated, including the change in entropy of nonregular condensed systems upon the introduction of polarizable charged polyatomic impurity particles into the system. To calculate the change in entropy of the system, the change in free energy of the system and its dependence on temperature are calculated.

To calculate the thermodynamic characteristics of condensed systems with impurity particles, we used the apparatus of temperature Green functions for nonregular condensed systems. The calculations took into account the effects of frequency and spatial dispersion of the system and the specific interactions of the impurity particles with the medium.

The paper notes that the main contribution to the change in the free energy of a system upon the introduction of an impurity into a condensed system is the electrostatic component associated with the interaction of the impurity particle with the environment. It is this change in the free energy of the system that provides the main contribution to the change in the entropy of the system, which is calculated in this paper.

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